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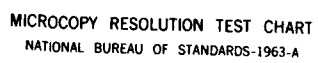
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Measurements made on the selected-ion flow-tube at the Air Force Geophysics Laboratory on the temperature dependence of several ion-molecule reaction rate coefficients. The N^+ + CO and C^+ + NO systems were studied over a range of 9 - 450° K. Measurements were also made on C^+ + O_2, CO^+ + O_2, and CO_2^+ + O_2 over the range 90 - 450° K. Comparison with available earlier results showed agreement within experimental uncertainty. A flowing afterglow apparatus was developed at Oklahoma for the study of ion interactions. Positive-ion/negative ion recombination was studied in this apparatus. Preliminary work was carried out for the Cl_2^+ + Cl system and photographic documentation is used to determine the strength of the recombination process.

$Cl_2(+)$

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

Our primary objective has been to complete data analysis and a journal publication on the temperature dependence of several ion-molecule reaction rate coefficients. The experimental work was carried out at the Air Force Geophysics Laboratory in collaboration with Dr. John F. Paulson.

The AFGL Selected-Ion Flow-Tube had not been used at temperatures other than 300°K previously. Relatively simple ion-molecule systems were chosen for this initial work. $N^+ + CO$ and $C^+ + NO$ were studied over the range 9-450°K in order to compare with recent beam-gas experiments at Universität Freiburg. In the case of $C^+ + NO$, the partial rate coefficients for the product channels had not been previously measured, even at room temperature.

We also made measurements on $C^+ + O_2$, $CO^+ + O_2$, and $CO_2^+ + O_2$ over the range 90-450°K. Previous work was at 300°K except for one $C^+ + O_2$ datum at 100°K, and high temperature data on $CO_2^+ + O_2$.

Where comparisons with earlier work were possible the agreement was within experimental uncertainties except for the product branching ratios measured in an ion cyclotron resonance apparatus by Anicich, Huntress, and Futrell for $C^+ + O_2$.

An article on these experiments and a detailed discussion of the results has been accepted by the Journal of Chemical Physics. Page proofs are attached to this report.

We have also continued our study of the perturbation of the gas flow in flow-tube reactors by high-speed helium injectors and have decided on a redesign of the injector which will eliminate a shock wave in the flow tube.

We have also completed the construction of a related apparatus at the University of Oklahoma for the study of ion interactions. This flowing afterglow apparatus is being used initially for research on positive-ion/negative-ion recombination. If the ion density is high enough ($\gtrsim 10^9$ cm^{-3}) the loss of plasma is dominated by ion-ion recombination, and a measurement of ion density vs flow time from a

reference point upstream in the apparatus yields the recombination rate. A mass spectrometer is used to identify the ion species present in the plasma at the dowstream end.

Preliminary work has been carried out for the simple $Cl_2^+ + Cl^-$ system. The attached photograph shows the apparatus in action. The bright white glow at the left is due to microwave excitation of the flowing helium gas. The blue glow just to the right follows injection of chlorine gas into the electron-ion plasma. Electrons rapidly attach to Cl_2 to form Cl_2^+. The blue glow is a result of electron transfer into excited states of Cl_2 via $Cl_2^+ + Cl^- ---> Cl_2^* + Cl --->$ $Cl_2 + Cl$ + light.

Thus, the rate of decay of the plasma which is evident in the photograph is indicative of the strength of the ion-ion recombination process. A langmuir probe is used to determine the ion density vs flow time (or distance). However, we have been using a monochromator to observe the light given off as an alternative measurement scheme. A number of advatages may ensue as outlined in our recent AFOSR proposal, "Experimental Studies of Atmospheric Ions: Ion-Ion and Photon-Ion Interactions", submitted in January, 1984.
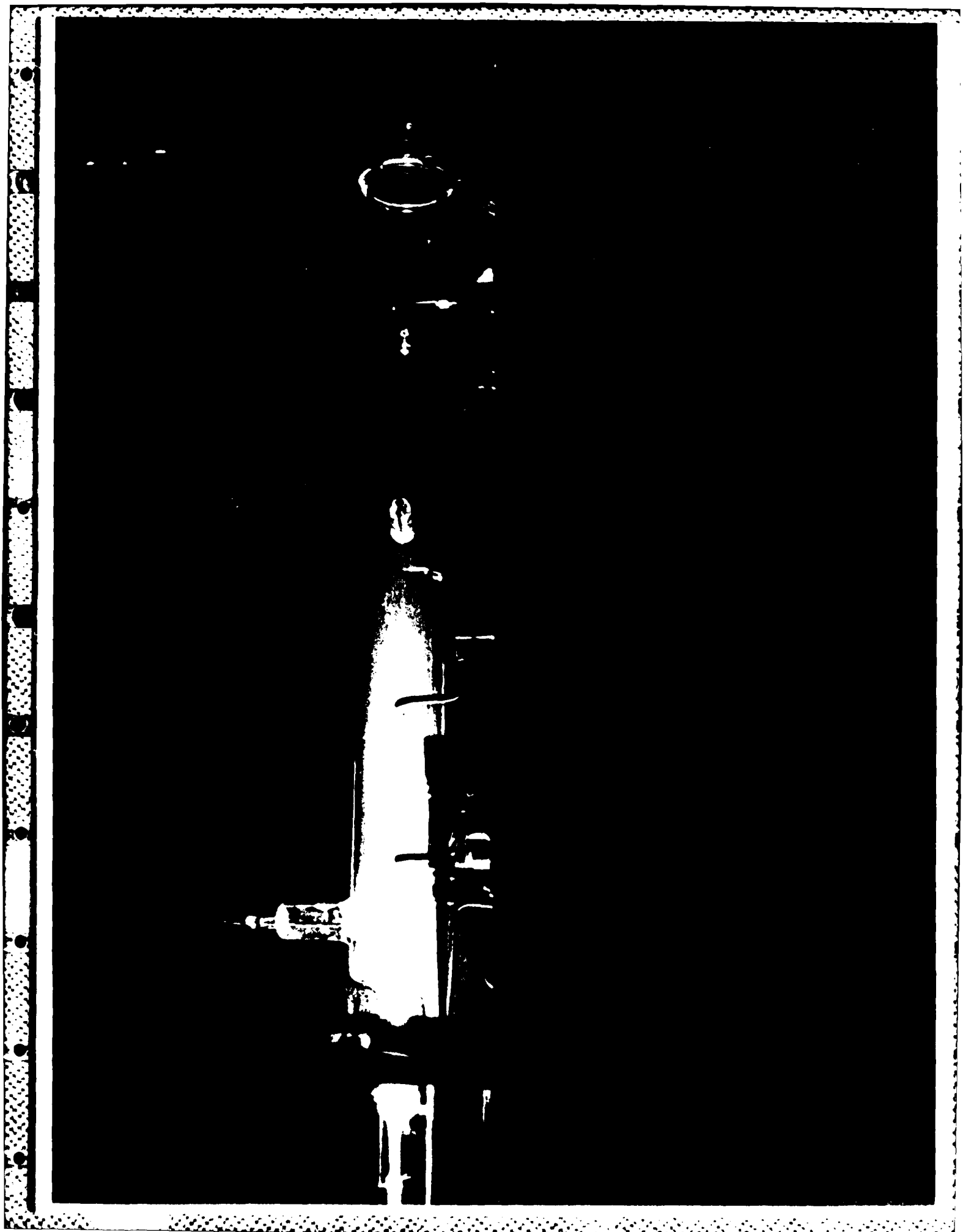
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Temperature dependence of the ion–molecule reactions N$^+$ + CO, C$^+$ + NO, and C$^+$, CO$^+$, CO$_2^+$ + O$_2$ from 90–450 K

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A variable-temperature, selected-ion flow tube was used to study the ion–molecule reactions N$^+$ + CO, C$^+$ + NO, C$^+$ + O$_2$, CO$^+$ + O$_2$, and CO$_2^+$ + O$_2$ over the temperature range of 90–450 K. We have measured reaction rate coefficients and have determined branching ratios for different reaction channels. The two C$^+$ reactions are found to be essentially gas kinetic in rate for 90–450 K. The other three reaction rate coefficients are found to decrease with temperature.

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I. INTRODUCTION

We have used a selected-ion flow tube to study several ion–molecule reactions as a function of temperature, over the range 90–450 K. We have studied the temperature dependence of reactions between N$^+$ + CO and between C$^+$ + NO in order to tie in with the remarkable supra-thermal data from Universität Freiburg.[1,2] Previous research on these two reactions has been carried out only at room temperature. Further, measurements of the product branching ratios were needed for comparison with the beam data. We have also studied reactions with O$_2$ for positive ions formed by electron impact on CO$_2$, namely C$^+$, CO$^+$, and CO$_2^+$,[3] in order to compare with previous data at one or more temperatures.[4-11]

II. EXPERIMENTAL APPARATUS, METHOD, AND ANALYSIS

The selected-ion flow tube (SIFT) apparatus was developed by Adams and Smith[12] at the University of Birmingham (UK) around 1975, an outgrowth of the well-established flowing afterglow technique[13] so successful at NOAA and elsewhere for the determination of ion–molecule reaction rate coefficients. The SIFT apparatus constructed at the Air Force Geophysics Laboratory and used in this work is similar to the variable-temperature version currently in use at the University of Birmingham.

Briefly, the AFGL SIFT apparatus consists of a 108 cm long, 7.3 cm i.d. stainless steel tube through which a helium carrier gas is flowed at low pressure (~0.3 Torr) and high speed (~10^4 cm/s). Ions are created in an electron-impact ion source, mass analyzed, and a current of ~10^{-10} A of a single desired ion species is injected into the flow tube at low energies (~20 eV) in the center of an annular jet of the helium carrier gas. The ions quickly thermalize in collisions with the helium gas and flow with the gas down the tube. The trip requires approximately 10 ms. At the end of this trip some of the ions pass through a small (0.03 cm) aperture leading into a second mass spectrometer maintained at high vacuum. The detected ion count rate is proportional to the original injected current.

The flow tube was cooled by bursts of liquid nitrogen through a copper jacket, or alternatively heated with car-

tridge heaters clamped to the jacket. The helium buffer gas was appropriately precooled or preheated.

In the ion source electrons were boiled off a thoriated-iridium filament in high vacuum and accelerated toward a gas cell where ions were produced by electron bombardment. N$_2$ gas was used for N$^+$ production, and CO$_2$ gas was used for C$^+$, CO$^+$, and CO$_2^+$. The electron acceleration potential was kept low enough that the apparent reaction rate coefficient was independent of the potential, i.e., presumably few metastable or doubly charged ions were produced. An acceleration potential of ~75 V was used for the results reported here.

The reaction rate coefficient was determined from the attenuation I/I_0 in the primary ion current reaching the detector, due to reactions with a density n of neutral reactants titrated into the helium buffer gas during a reaction time t:

$$k = \ln(I_0/I)/nt. \qquad (1)$$

Experimentally, the small concentration n of the reactant gas was determined from the measured helium density N and the throughput Q_R of the reactant gas compared to the helium throughput Q_{He}. The reaction time t was determined from a direct measurement of the ion velocity v_i and of the distance d over which the reactant gas flows. Thus,

$$k = \frac{\ln(I_0/I)}{(Q_R N/Q_{He})(d/v_i)}. \qquad (2)$$

In practice, approximately ten values of I were obtained for corresponding values of n (or Q_R), for each of three reaction distances d (74.0, 43.5, and 28.3 cm).

Product ion currents were also recorded for each value of n so that the product ion percentages could be determined (extrapolating to $n = 0$). A product of a *secondary* reaction is easily identified with this procedure since the product percentage extrapolated to $n = 0$ is zero for a secondary product.[12]

The ion velocity was determined from time-of-flight measurements. An electrode in a side port half-way down the flow tube could be biased so as to pull the ions out of the helium flow. When this electrode was pulsed to zero potential for 0.1 ms, a pulse of ions was allowed to pass down the second half of the flow tube and their arrival time at the detector was measured. It is known from the work of Ferguson *et al.*[13] and of Adams *et al.*[14] that the ion velocity v_i is greater than the bulk helium velocity v_{He} since the ion den-

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sity is greatest near the flow tube axis where the helium ve-locity is greatest. In our apparatus $v_i/v_{He} = 1.68$ above room temperature but the ratio increased with lower temperatures, reaching 2.1 at 90 K. These values are independent of the flow tube pressure.

We observed the effect of a shock wave associated with the helium injection. If the pressure drop across the injector was too large the resulting shock affected the helium flow far enough downstream to interfere with our measurements when using the longest reaction path. The disturbance of the helium flow could most easily be seen in the ion time-of-flight data. We were able to measure the ion flight time for both the first half of the flow tube and for the second half of the flow tube length. The former indicated a much larger ion speed near the helium injector and v_i/v_{He} depended on the pressure drop across the injector. The latter, used in our reaction data analysis, gave ratios v_i/v_{He} which were pressure independent. For low pressure differentials the ion speed was constant over the entire length of the flow tube. Our observations are consistent with the studies of Dupeyrat et al.,[15] who concluded as we do that the shock wave is inconsequential to the reaction data provided that adequate distance is allowed for equilibrium flow to be established. It is perhaps advantageous to have the helium injector not directed down the flow tube axis, but rather at an angle to the flow tube axis ($\sim 30°$ for Adams and Smith[12]), and to design the helium injector so as to have a small pressure drop across its opening.

We have uncertainties in the quantities in Eq. (2) as follows: $\sim 2\%$ in each of d, v_i, and Q_{He}, and $\sim 10\%$ uncertainty in the capillary-flow calibration for Q_R. Considering statistical variations in the data, we believe that the reaction rate coefficients presented here are accurate to within 25%. The temperatures were measured with five platinum resistance thermometers along the flow tube and these generally agreed within 5 K. At our highest temperature a variation as great as 20 K was indicated because we were unable to pre-heat the helium buffer gas adequately.

III. DISCUSSION OF RESULTS

A. $N^+ + CO$

The reaction $N^+ + CO$ was found to have a reaction rate coefficient which decreases with temperature, as shown in Fig. 1. At our lowest temperature 88 K, the reaction rate coefficient is approximately equal to its gas kinetic value[16] of 1.1×10^{-9} cm³/s. At our highest temperature 454 K, the reaction rate coefficient has dropped to about half the gas kinetic value. Charge transfer dominates ($\sim 85\%$) at all temperatures studied and is exoergic by 0.52 eV. The only other exoergic channel is $N^+ + CO \rightarrow NO^+ + C + 0.65$ eV, which we observe taking place whenever charge transfer does not occur. Our product percentages are accurate only to within about five percentage points.

Our measured rate coefficients, in units of 10^{-10} cm³/s, are: 9.7(88 K), 7.2(146 K), 6.7(196 K), 6.3(245 K), 5.9(296 K), 5.3(371 K), and 4.6(454 K). Our room temperature result is 31% higher than that of Smith et al.[17] and 8% lower than that of Lindinger,[18] 18% higher than that of Fehsenfeld et
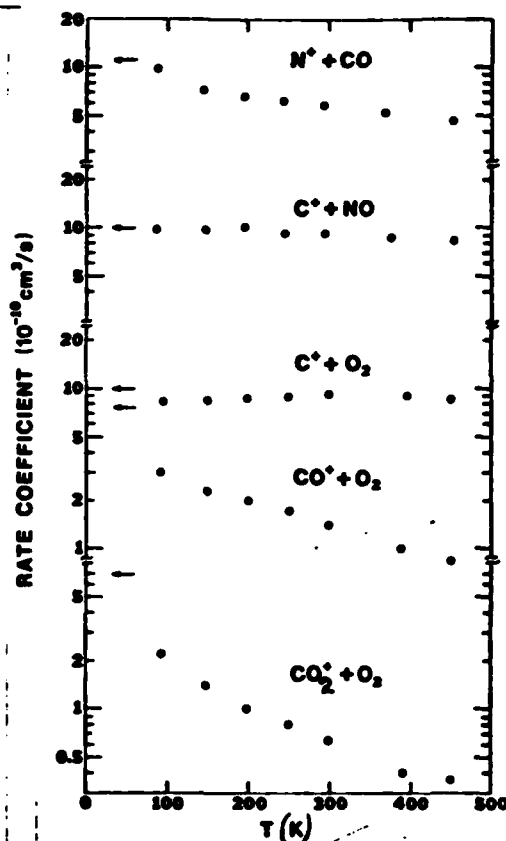

FIG. 1. Measured reaction rate coefficients vs temperature. The vertical scale is broken as indicated to avoid overlapping of data points. The arrows give the gas kinetic rate coefficient (Langevin or average-dipole-orientation model) in each case, calculated using formulas in Ref. 16.

al.,[19] and 37% higher than that of Tishy et al.,[20] but is within the combined uncertainties of the experiments. The flow-drift tube data of Lindinger[18] show a decrease in k with the center-of-mass kinetic energy ($KE_{c.m.}$) which is consistent with the decrease in k vs temperature which we observe. It is, of course, difficult to make a direct comparison between temperature and relative energy in the flow-drift tube.

Frobin, Schlier, Strein, and Teloy[1] have studied this reaction by interacting a low-energy N^+ beam with CO gas and collecting and mass analyzing all of the product ions. At sufficiently high energies (several electron volts) all possible product ions are observed by Frobin et al. The cross sections for the exoergic channels (producing NO^+ and CO^+ ions) show minima, apparently the result of a decrease in the very low energy "capture" cross section versus $KE_{c.m.}$ and the rise from threshold of the "direct reaction" cross section. At their lowest energy ($KE_{c.m.} = 0.13$ eV) Frobin et al.[1] measure the product branching ratio as $\sim 11\%$ NO^+ and $\sim 89\%$ CO^+, which agrees with our result and others.[17,18]

Guyer, Hüwel, and Leone[21] have used a crossed-beam apparatus to study the partition of energy in the $N^+ + CO \rightarrow CO^+ + N$ reaction. The 0.52 eV exoergicity allows the product CO^+ to be vibrationally excited up to $v'' = 2$. The CO^+ vibrational excitation observed by Guyer et al. in this reaction is approximately that predicted by a Franck–Condon analysis. Guyer et al. found that for $v'' = 0$

the rotational temperature was only 410 K, implying that almost all of the exoergicity of the reaction went into translational energy of the products.

B. C^+ + NO

The reaction C^+ + NO proved to be near its gas kinetic rate of about 1.0×10^{-9} cm³/s for temperatures of 90–300 K, but decreased slowly at higher temperatures. Charge transfer is exoergic by 2.00 eV and we find it to dominate (92%) at all temperatures studied. There are two other exoergic reaction channels. C^+ + NO→CO^+ + N is exoergic by 1.87 eV and we observe it in about 8% of the reactions occurring. C^+ + NO→CO + N^+ is energetically allowed (by 1.35 eV), but we see only trace amounts of N^+(0.1%) which although correlated with NO concentration could not be shown to be a definite product of the C^+ + NO reaction. The few N^+ ions observed might well be produced through impurities or in surface reactions on the walls of the flow tube.

Our rate coefficient, in units of 10^{-10} cm³/s, are: 9.8(88 K), 9.8(148 K), 10.2(196 K), 9.3(247 K), 9.4(297 K), 8.7(377 K), and 8.3(453 K). The only other thermal-energy studies of C^+ + NO of which we know are those of Anicich et al.,[9] Tichy et al.,[20] and the preliminary work of St. Niccolini et al.[11] Anicich et al.[9] find a reaction rate coefficient of 8.5×10^{-10} cm³/s in an ion cyclotron resonance apparatus with ion energies <0.1 eV. Tichy et al.[20] used a SIFT apparatus and measured a rate coefficient of 6.9×10^{-10} cm³/s with charge transfer occurring in most of their reactions. Tichy et al. did not observe the CO^+ + N channel. We have carefully studied the product distribution measurements and cannot explain this discrepancy. St. Niccolini et al.[11] used a drift tube apparatus and reported a value of 5.7×10^{-10} cm³/s at room temperature, with NO^+ as the major product. The reaction rate coefficient was found by St. Niccolini et al. to decrease slowly with $KE_{c.m.}$.

Cahnbley, Schlier, and Teloy[2] have studied this reaction in the beam-gas apparatus mentioned earlier. As before, at sufficiently high energies they observe all possible ion products and have obtained the individual reaction cross sections. Their experiment extends to low enough energies ($KE_{c.m.}$ = 0.04 eV) that the capture cross sections for the exoergic channels are significant. Cahnbley et al. find the branching ratio at very low energies to be 98% NO^+, 1.5% CO^+, and 0.16% N^+, with the CO^+ fraction consistently decreasing with decreasing $KE_{c.m.}$. Cahnbley et al.[2] point out that a crossing between the NO + C^+ and NO^+ + C potential curves can account for the dominance of the charge transfer channel in their experiments.

We observe a larger fraction of the CO^+ product (8 ± 5)% in our experiment at thermal energies than one would expect from the results of the beam experiment, and we see essentially no change in the branching ratio over 90–450 K. A significant CO^+ product fraction is somewhat surprising since there is no adiabatic correlation[1,2] between the reactant C^+ + NO and the product N + CO^+ (for ground-state CO^+, the only exoergic possibility). Frobin et al.[1] found that the results of their study of N^+ + CO collisions could be explained qualitatively on the basis of adiabatic correla-

tions of collinear potential surfaces. An exception was the charge transfer channel, for which a diabatic connection between N^+ + CO and N + CO^+ was required. In their analysis of the reaction C^+ + NO→N + CO^+, Cahnbley et al.[2] speculate that the low energy production of CO^+ is possibly due to the same N^+ + CO→N + CO^+ diabatic transition. (At higher energies, excited CO^+ is adiabatically allowed.)

C. C^+ + O_2

The interaction C^+ + O_2 proved to be relatively independent of temperature over the range 90–450 K and only slightly lower than the calculated gas kinetic (Langevin) rate coefficient of 1.0×10^{-9} cm³/s. Simple charge transfer is endoergic (by 0.80 eV) in this case. Two other reaction channels were observed, however. The first, C^+ + O_2→O^+ + CO is exoergic by 3.64 eV, and is favored (62%) at all temperatures used. Although the neutral CO product is not observed directly, the energetics of the reaction require that it be bound. The second channel observed is C^+ + O_2→CO^+ + O, which is exoergic by 3.24 eV.

Our results for the reaction rate coefficient are shown in Fig. 1 and, in units of 10^{-10} cm³/s, are: 8.3(96 K), 8.5(150 K), 8.8(200 K), 9.0(250 K), 9.3(300 K), 8.9(395 K), and 8.5(450 K). Our 300 K datum may be compared to the value obtained by Adams and Smith,[4] 9.9×10^{-10} cm³/s, and to that obtained by Rakshit et al.,[5] 9.0×10^{-10} cm³/s. Rakshit et al. also found 9.0×10^{-10} cm³/s at 100 K. Tichy et al.[20] found a lower rate coefficient, 7.4×10^{-10} cm³/s at 300 K, and nearly equal product percentages for O^+ + CO and CO^+ + O. Our product distribution is the same as that reported by Adams and Smith.[4] St. Niccolini et al.[11] have given preliminary results which likewise show the same product distribution at 300 K. By increasing $KE_{c.m.}$ with an electric field they find that the product distribution gradually approaches 50% O^+ and 50% CO^+ at relative energies of ~1 eV.

Anicich et al.[9] found 12.2×10^{-10} cm³/s for this reaction in an ion cyclotron resonance apparatus with ion energies <0.1 eV. Oddly, the product distributions reported by Anicich et al. are exactly the opposite of what we and others[4,11] have found. (They reported 35% O^+ and 64% CO^+ products, with an estimated uncertainty of three percentage points.) This discrepancy cannot be explained by the presence of nonthermal ions in the ICR cell because St. Niccolini et al.[11] show the O^+ product to be the dominant one at energies up to 1 eV, after which the 50–50 ratio obtains.

D. CO^+ + O_2

The rate coefficient for the charge transfer reaction CO^+ + O_2→CO + O_2^+ was found to increase with decreasing temperature, approaching the calculated gas kinetic rate of 7.7×10^{-10} cm³/s at very low temperatures. This reaction is exoergic by 1.95 eV.

Our results for the reaction rate coefficient, in units of 10^{-10} cm³/s, are: 3.1(92 K), 2.3(150 K), 2.0(200 K), 1.7(250 K), 1.4(300 K), 1.0(388 K), and 0.82(450 K). Our 300 K datum may be compared with the value obtained by Adams, Smith, and Grief,[6] 1.2×10^{-10} cm³/s.

E. $CO_2^+ + O_2$

The rate coefficient for the charge transfer reaction $CO_2^+ + O_2 \rightarrow CO_2 + O_2^+$ was likewise found to increase with decreasing temperature, approaching the calculated gas kinetic rate of 6.9×10^{-10} cm³/s at very low temperatures. Our data join smoothly onto the high temperature data of Lindinger et al.,[7] which extend to 900 K and show that the rate coefficient passes through a minimum in the neighborhood of 680 K, implying that other reaction channels (probably due to vibrational excitation) become effective at higher temperatures. The charge transfer reaction is exoergic by 1.71 eV. All rearrangement reaction channels are forbidden energetically in our temperature range.

Our results for the reaction rate coefficients, in units of 10^{-10} cm³/s, are: 2.2(94 K), 1.4(148 K), 1.0(198 K), 0.80(250 K), 0.63(300 K), 0.40(391 K), and 0.36(450 K).

ACKNOWLEDGMENTS

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